

# Transition between graphene-film and carbon-nanotube growth on Nickel alloys in open-atmosphere flame synthesis

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## ABSTRACT

Using open-atmosphere flame synthesis, graphene films and carbon nanotubes (CNTs) are grown directly on nickel and nickel-alloy substrates. The gas-flow input CH<sub>4</sub> to H<sub>2</sub> ratio (1:10) is held constant. For nickel, copper–nickel, and Inconel, few-layer graphene (FLG) grows at 850 °C. Transitional growth from FLG to CNTs is observed on nickel, copper–nickel, and Inconel, as the substrate temperature is decreased to 500 °C. CNT growth is found for nitinol at 500 °C; however, graphene growth is not observed for nitinol at elevated temperatures for the examined experimental conditions.

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## 1. Introduction

Allotropes of carbon, for example graphene and carbon nanotubes (CNTs), are the subject of intense scientific interest. Graphene and CNTs, comprised of sp<sup>2</sup>-bonded carbon atoms, exhibit remarkable electrical and mechanical properties, with the potential to replace silicon in electronic devices [1,2]. The growth of carbon nanomaterials on metals has been well studied using chemical vapor deposition (CVD). Graphene can be grown on copper (Cu) [3] and nickel (Ni) [4] foils at temperatures ~1000 °C. Temperature and substrate composition are of critical importance in the growth of graphene [5,6]. For CNTs, the substrate is normally seeded with catalytic nanoparticles (Ni, Co, or Fe), with a typical growth temperature ~500 °C [7]. While conventional CVD has emerged as the leading technology for the production of graphene and CNTs, the process can be costly, require lengthy processing times, and be restricted to confined synthesis.

A common requirement in the growth of carbon nanomaterials is a carbon feedstock and heat. Flame synthesis offers the advantage of efficiently providing both elevated temperature and precursor carbon species for growth. Recently, we reported the growth of few-layer graphene (FLG) films on Cu and Ni substrates using flame synthesis [8,9] in open environments. The growth of CNTs [10–12] using flame synthesis has been widely demonstrated; however, this work evinces that by varying the temperature, growth can readily transition between CNTs and FLG. Additionally, while the growth of CNTs has been demonstrated on a number of Nickel alloys [10,11,13] (i.e. Cu–Ni, Ni–Fe–Cr, Ni–Ti, and Co–Ni), the growth of graphene has only been previously demonstrated on Cu–Ni [14]. Finally, our system requires no prior substrate preparation, permits

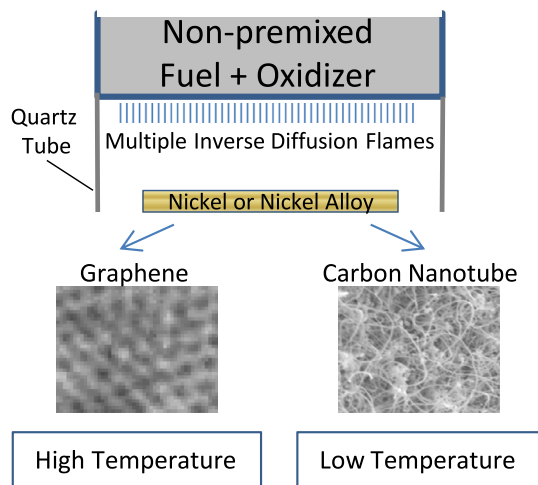
open-environment processing without a confining chamber, affords high growth rates (minutes versus hours as compared to other methods), and can be economical in that the fuel serves both as heating source and reagent.

## 2. Experiment

In our setup (Figure 1), the pyrolysis gases of multiple inverse-diffusion flames [8,9] impinge on a substrate, enabling the growth of carbon nanomaterials. The burner operates in an inverse mode, where for each distinct flame in the planar array, oxidizer is in the center, and fuel (e.g. H<sub>2</sub>, CH<sub>4</sub>) surrounds it [8], with the under-ventilated flame enveloping the oxidizer flow. This design results in: (i) input oxygen being completely consumed, (ii) large quantities of hydrogen and carbon-rich species being generated, and (iii) radially uniform scalar properties being established axially downstream. Ni, Cu–Ni (Ni 67% wt, Cu 33% wt), Inconel 600 (Ni 72% wt, Cr 16% wt, Fe 12% wt), and nitinol (Ni 55% wt, Ti 45% wt) are investigated as substrate materials. The carbon solubility of Ni and other metals used as alloys in the study are given in Table 1. Prior to any carbon-based synthesis, the metal substrates are subjected to the burner operating under globally-rich hydrogen conditions for 10 min, to reduce any oxide layers on the surface. Subsequently, CH<sub>4</sub> is introduced (with a global equivalence ratio of ~3) for 5–10 min. The growth temperature is the same as the reduction pre-treatment temperature. At a temperature of ~200 °C, nickel-oxide reduces to Ni in an H<sub>2</sub> environment [15]. Therefore, the difference in the reduction temperature between the low-temperature (500 °C) and high-temperature (850 °C) cases is not expected to significantly influence the obtained structures. The gas input ratio between CH<sub>4</sub> and H<sub>2</sub> is kept constant at 1:10. For a fixed substrate distance of 15 mm downstream from the burner exit, the temperature of the substrate is varied from 850 to

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**Figure 1.** Schematic diagram of the experimental setup. The substrate (Ni, Cu–Ni, Inconel, or nitinol) is held at a high temperature (850 °C) or a low temperature (500 °C).

500 °C, and is measured using both thermocouple and pyrometer. Although the flame temperature is kept constant, the type and concentrations of the carbon and hydrocarbon species (e.g. CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, PAHs, etc.) at the substrate could differ for different surface temperatures. Thus, future work will involve measuring the species concentrations using laser-based diagnostics to determine explicitly the local growth conditions.

### 3. Results and discussion

Raman spectroscopy identifies FLG [16], where the first order Raman spectra is comprised of the D, G, and 2D bands, which are located at shifts of  $\sim 1350$ ,  $\sim 1580$ , and  $\sim 2700$  cm<sup>-1</sup>, respectively [17]. For Ni, the growth of FLG growth occurs at 850 °C (Figure 2a). Characterization using TEM corroborates the growth of FLG (Figure 2b). At 850 °C, no CNTs are grown on Ni for fixed flame conditions, as verified by FESEM (Figure 2c). The darker areas shown in Figure 2c are where FLG has detached locally from the substrate, probably due to a combination of growth stresses and thermal expansion misfit stresses during cooling after deposition. These effects are dependent on film thickness, where fewer layers are less disposed to film delamination. When the substrate temperature is lowered to 500 °C, multi-wall carbon nanotubes (MWNs) are observed, as shown in Figure 2d. The direct growth of CNTs using bulk metals involves initial catalytic nanoparticle formation on the substrate followed by initiation and growth [12]. Nanoparticle formation on bulk metals can be due to carbide-induced breakup of the substrate or mechanical roughening. However, at 500 °C the

carbon solubility in Ni is minimal; hence, nanoparticle formation likely occurs during the hydrogen flame reduction of the thin oxide layer on the Ni substrate. A critical parameter that determines the growth of graphene versus CNTs is related to the carbon solubility of the bulk metal. At high temperatures, carbon atoms are soluble in Ni [18]; and upon cooling, the carbon precipitates out to form FLG. In contrast, at low temperatures, hydrocarbon pyrolysis gases adsorb on the substrate, leading to the formation of CNTs [19].

CVD growth of graphene on metals involves high substrate temperatures, which are necessary for hydrocarbon dissociation within the thermal boundary layer. Lower temperature growth is important for industrial feasibility and economic cost. In our setup, combustion provides hydrocarbon dissociation such that post-flame gases are comprised of relevant carbon-rich pyrolysis species (such as CO and C<sub>n</sub>); thus high substrate temperatures are not necessary for graphene growth. Figure 3 shows the Raman spectrum of the graphene growth on Ni at different temperatures. The growth of FLG is observed at 750 and 600 °C, without the presence of CNTs. At 600 °C a higher D peak is observed (Figure 3), which is related to the disorder present in the graphene film. A larger disorder peak is typically encountered in the low temperature growth of graphene [20]. The growth of CNTs on Ni is only observed at temperatures starting at  $\sim 500$  °C, where a small 2D peak is observed in the Raman spectrum, as seen in Figure 3.

The carbon solubility of a metal plays a critical role in the growth of graphene. Copper, due to its low carbon solubility, is an ideal metal for limiting the growth of graphene layers [8]. Using alloys such as Cu–Ni can enable the adjustment of the overall carbon solubility, as shown in Table 1, and thus can be important in the optimization of graphene synthesis [14]. The Raman spectrum, as seen in Figure 4(a), confirms the growth of FLG on Cu–Ni at a temperature of 850 °C. The disorder (D) peak is higher for Cu–Ni as compared to that for Ni. From FESEM (Figure 4b), no CNTs are observed at this temperature. When the temperature of the Cu–Ni substrate is lowered to 600 °C, CNTs are found on the substrate, as seen in Figure 4c, growing from the grain boundaries. Higher yields of CNTs occur at a temperature of 500 °C for Cu–Ni (Figure 4d). Hydrogen etching produces small Ni nanoparticles on pure Ni [21]. Due to the formation of numerous Ni nanoparticles, a higher yield of CNTs and wider temperature range for growth is observed on the Cu–Ni, as compared to that for pure Ni. In the intermediate case, densely packed nucleation of nanoparticles seems to occur at the grain boundaries, as large quantities of CNTs are visible near them (Figure 4c). Compared to single metals, alloys are known to increase the yield of CNTs, and have higher carbon solubilities (due to lattice misfits). Grain boundaries are more susceptible to carbon uptake and carbide formation, which occurs at low temperatures, rather than at high temperatures due to the weakly formed bond. As such, carbide-induced breakup (due to volumetric lattice mismatch between the carbide and the surrounding metal) is facilitated there, promoting nanoparticle formation, catalyzing CNT growth. No growth of CNTs occurs at 850 °C on Cu–Ni, as carbon atoms are very soluble within Ni at 850 °C, poisoning CNT growth, and instead resulting in the formation of FLG upon cooling.

Next, the transitional growth between graphene and CNTs is investigated on Inconel and nitinol. At a temperature of 850 °C, the growth of FLG is observed on Inconel (Figure 5a). Exclusive growth of FLG is not observed on nitinol for the examined experimental conditions. Although carbon is highly soluble within Ni–Ti [22], TiC<sub>1-x</sub> readily forms [13], which can break up the substrate surface. This results in a disordered structure at a temperature of 850 °C, as shown in Figure 5b. When the temperature is lowered to 500 °C, the growth of CNTs is verified on Inconel and nitinol using FESEM, as seen in Figure 5c and d, respectively. The yield of CNTs, as assessed from FESEM, is noticeably lower on the pure

**Table 1**

Carbon solubility of Ni and the other metals whose alloys are used in the growth of graphene and CNTs [6,24].

Metal or alloy	Carbon solubility (maximum)	Melting point (°C)
Ni	2.7 at.%	1455
Cu–Ni alloy <sup>a</sup>	0.04–2.7 at.%	1085–1455
Fe <sup>b</sup>	$\sim 7.5$ at.% ( $\gamma$ ) <sup>b</sup>	1538
Ti <sup>c</sup>	$\sim 1.8$ at.% ( $\beta$ ) <sup>c</sup>	1668

<sup>a</sup> Properties vary according to the atomic ratio of Ni and Cu.

<sup>b</sup> Carbide formation (e.g. Fe<sub>3</sub>C) with  $>25$  at.%.

<sup>c</sup> Carbide formation (e.g. TiC<sub>1-x</sub>) with  $>30$  at.%.

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